Effect of synthesis parameters on the thermal behaviour of yttrium and iron amorphous oxides prepared by coprecipitation.

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Introduction

As part as of an overall research subject to control the densification of yttrium iron garnets prepared by coprecipitation [1..4], we have studied the thermal behaviour of the hydroxide obtained at the end of the synthesis.

The use of thermal analysis methods such as differential thermal stability (DTA) and high temperature X-rays diffractometry (HTXRD) allows us to show the effect of some synthesis parameters on the crystallization of the yttrium iron garnet. The observed phenomena can be related to the presence of the anions which stay in the solid.

I. Elaboration process

The samples are prepared by coprecipitation of hydroxides. This is carried out by injecting a solution containing yttrium and iron salts (where $[Fe^{3+}]/[Y^{3+}] = 5/3$) into an ammonia solution whose pH is regulated. Figure 1 shows the experimental apparatus used for the preparation of the coprecipitates.

A solution of 250 ml is prepared which contains iron and yttrium salts and has a concentration of cations of 1 mol/l is continuously.stirred A 3000 ml ammonia solution is placed into a 25°C thermostated reactor and is agitated throughout the whole operation. Two peristaltic pumps are used to add the solution of the salts to the ammonia solution and also to maintain the pH at a constant value by addition of a concentrated NH_4OH solution. The coprecipitate is then separated from the solvant by centrifugation.

The obtained gel can be washed once or several times with 3000 ml of deionized water during 1 hour in the thermostated reactor in order to remove any ammonium nitrate which might be present. After the last washing operation, the gel is dried and then blended in order to obtain a finely divided powder (figure 2).

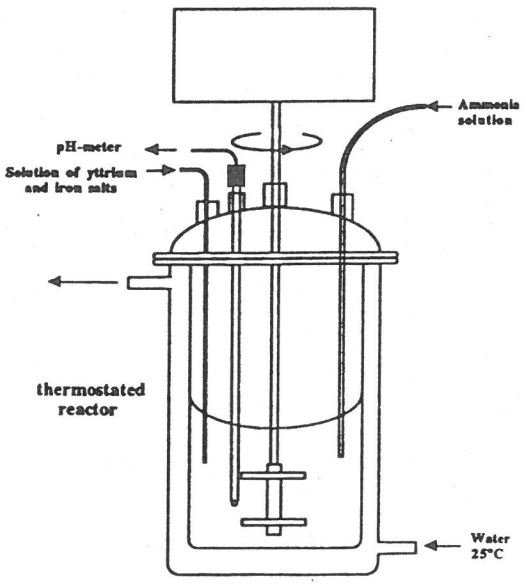


Fig. 1. Experimental apparatus used for the preparation of the coprecipitates

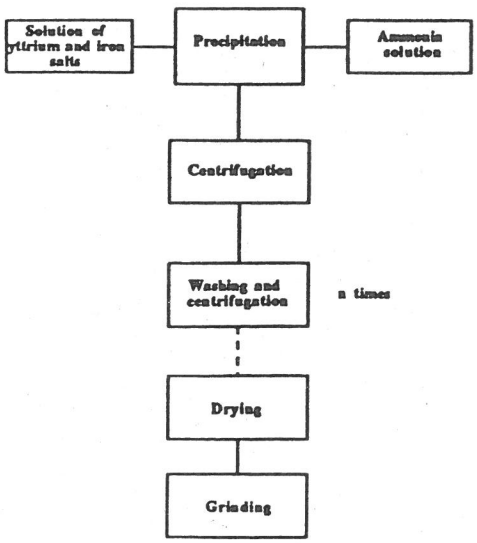


Fig. 2. Elaboration process

II. Analysis of gel thermal behaviour

Figure 3 shows the general appearance of DTA curves obtained from the coprecipitates. This curve is measured for an unwashed gel prepared by coprecipitation from nitrate salts at a pH of 10.5. It reveals the existence of four thermal effects which we can attribute to the following phenomena:

1. between 100°C and 200°C: endothermic peaks caused by the desorption of water and by the decomposition of the hydroxide
2. at around 330°C: endothermic peak due to the decomposition of NH_4OH
3. at around 420°C: endothermic peak due to the decomposition of nitrates
4. between 750°C and 850°C: exothermic peaks related to the cristallization.

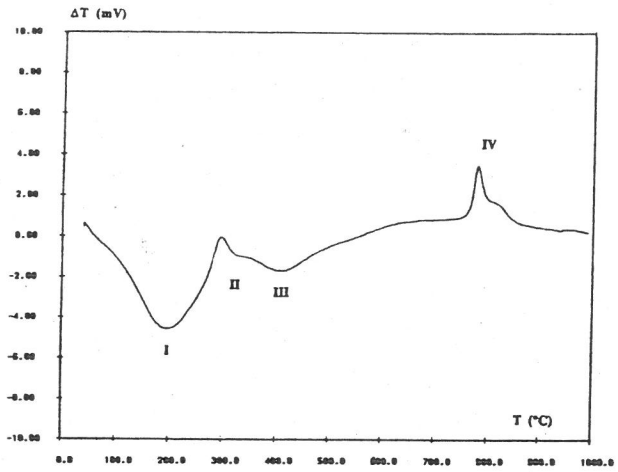
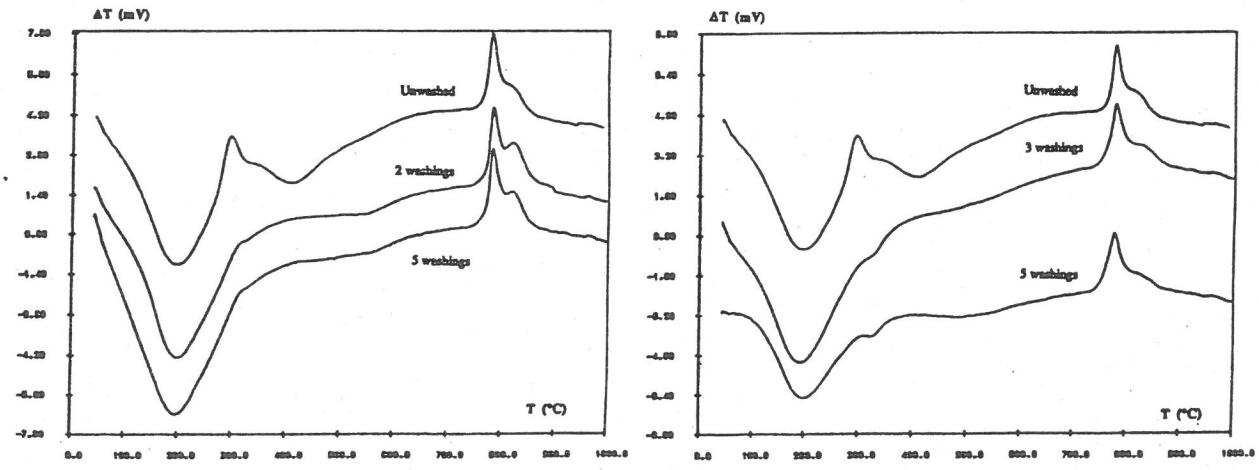


Fig. 3. DTA curve obtained for an unwashed gel

Differential thermal analysis can be used to intrepret the peaks 2 and 3. We observe a decrease in the intensity of both peaks when the samples are washed with deionized water; however, only peak 3 decreases when they are washed with an ammonia solution of pH 10.5 (figure 4).



a) b)

Fig. 4. Variation of DTA curves as a function of the number of washings, with: a) H_2O; b) NH_4OH solution of pH 10.5

It seems that the crystallization is the most interesting of the phenomena as it is characterized by the presence of two exothermic peaks which depend strongly on the parameters of the coprecipitate preparation. Figure 5 shows that the peak temperatures increase with the number of washings which leads to a separation of the peaks.

HTXRD analysis is used to show that two different crystallized phases are formed: the garnet $Y_3Fe_5O_{12}$ and the perovskite $YFeO_3$. The amount of perovskite formed is higher for a washed gel than for an unwashed one (figure 6).

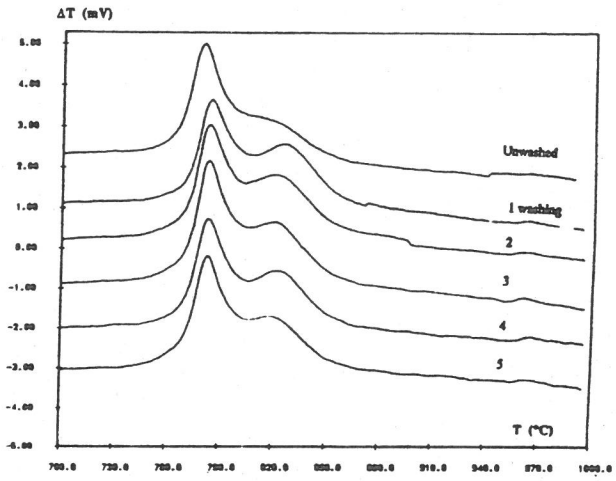


Fig. 5. Effect of washings with H_2O on the exothermic peaks due to the crystallization

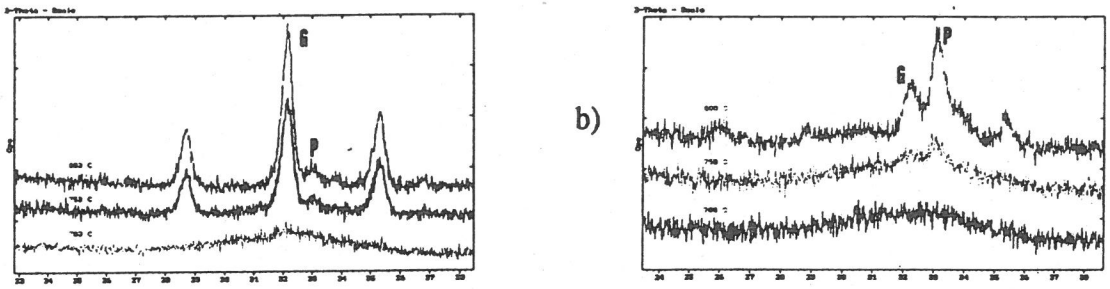


Fig. 6. HTXRD diffractograms as a function of T (°C) for:
a) unwashed gel and b) gel that have been washed four times

The type of yttrium and iron salts used is another parameter which has an influence upon the crystallization. Some authors who have previously synthetized gels from YCl_3 and $FeCl_3$ have noted that the crystallization shows up as one exothermic peak at around 730°C [5,6].The same effect can be observed if the gel which is prepared from nitrate salts and washed four times is doped with a NH_4Cl solution. The DTA curve obtained in this case is comparable to the results found in litterature (figure 7).

We can conclude that the crystallization of amorphous mixed oxide of yttrium and iron with $[Fe^{3+}]/[Y^{3+}] = 5/3$ largely depends on the synthesis conditions. It appears that the anions which are present in the solid during heat treatment have an important influence corresponding to their type and their concentration. This presence inhibits the demixtion which arises during the crystallization.

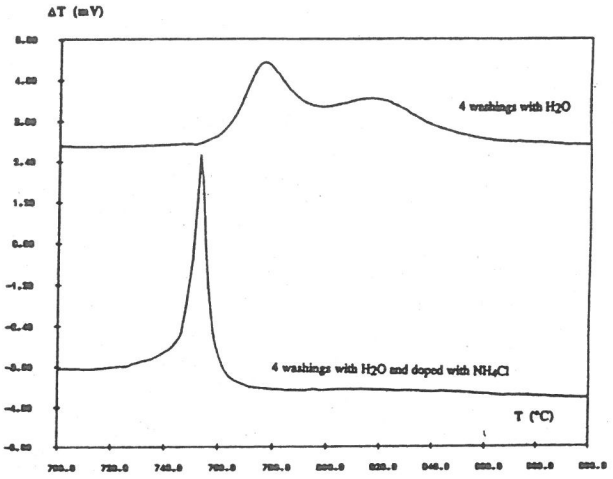


Fig. 7. DTA curves for coprecipitate from nitrates which are undoped and doped with a solution of NH_4Cl

III. Preparation of $Y_3Al_xFe_{5-x}O_{12}$ compounds

Al substituted garnets are widely used in the construction of microwave devices.

We have prepared sample of such compounds by coprecipitation from nitrates. The prepared compounds have a formula of $Y_3Al_xFe_{5-x}O_{12}$ where $0 \leq x \leq 1$.

The powders are elaborated in the same manner as described above but at pH = 10 and by washing five times with deionized water and then three times with ethanol for 15 min.

DTA curves measured for those coprecipitates show that one of the two exothermic peaks disappears as the value of x increases (figure 8). This result is confirmed by HTXRD analysis which reveals that the formation of the perovskite phase is inhibited by the presence of Al^{3+} ions in the structure (figure 9).

Such a behaviour could be related to the fact that the perovskite formation becomes thermodynamically less favorable as the value of x increases. However, we can conclude that the demixtion observed above is not a result of a loss of homogeneity during washing.

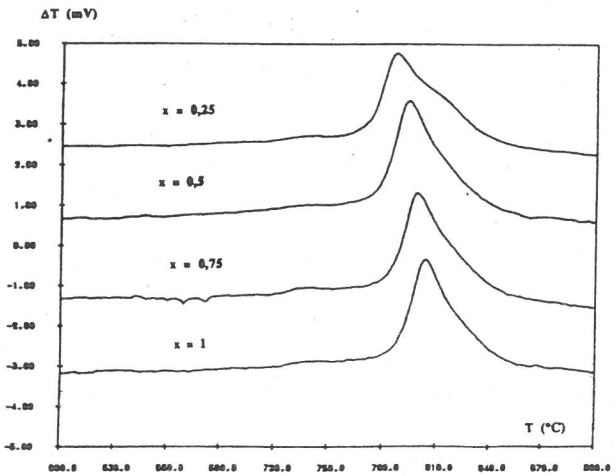
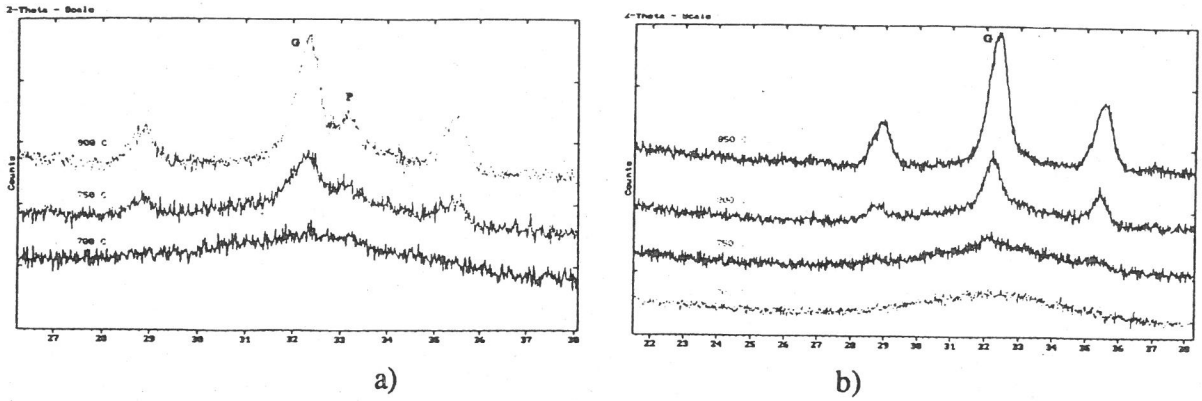


Fig. 8. Effect of the Al substitution on the crystallization



a) b)

Fig. 9. Effect of Al substitution on the phases formed during the crystallization for: a) x = 0.25; b) x = 0.75

Conclusion

This work shows that simple analysis methods such as DTA and HTXRD can be useful in the study of crystallization. However, we are unable, at this time, to explain the experimentally observed results and to interpret the intervention of the anions.

We can measure the complexity of chemical route elaboration processes. This is illustrated by the existence of many parameters which must be mastered in order to control the reactivity of the powders prepared.

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